

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : TONEN CHEM CORP

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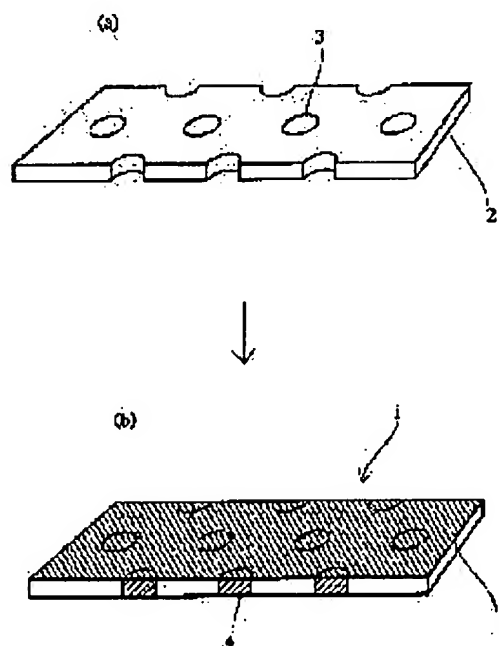
(72)Inventor : YAMAGUCHI TAKEHISA
NAKAO SHINICHI
KIMURA HISAFUMI

(54) SEPARATION MEMBRANE, ITS PRODUCTION AND SEPARATION METHOD

(57)Abstract:

PURPOSE: To obtain a separation membrane capable of selectively removing an org. compound dissolved in water by performing the graft polymerization of a water-insoluble monomer on a polyethylene microporous membrane to substantially fill the pores of the microporous membrane with the graft polymer of the water-insoluble monomer.

CONSTITUTION: A uniform water-insoluble monomer emulsion is prepared by adding 0.1-100 pts.wt. of a water-insoluble monomer (e.g. ethyl acrylate) to 100 pts.wt. of water containing 0.1-50wt.% of a surfactant (e.g. sodium dodecylbenzenesulfonate). Next, a polyethylene microporous membrane 2 having a radical formed by the irradiation with plasma is brought into contact with the emulsion and the pores 3 of the membrane 2 are substantially filled with the graft monomer 4 of the water-insoluble monomer to prepare a separation membrane 1. An org. compound (e.g. chloroform) dissolved in water can be selectively removed by the separation membrane.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the demarcation membrane which can carry out separation removal of the organic compounds, such as trihalomethane contained especially underwater, alternatively, its manufacture approach, and the separation approach using such a demarcation membrane about the separation approach which used a demarcation membrane, its manufacture approach, and a demarcation membrane.

[0002]

[Description of the Prior Art] The membrane-separation method for separating various mixture using the film which has pore becomes more prosperous recent years still, and the technique is being applied in various fields. Moreover, the separation object in a membrane-separation method was also crossed to not only solid-state-liquid mixture but liquid-liquid, gas-gas, and gas-liquid mixture, and the large range, and interests have gathered for development of the demarcation membrane and separation technology to various mixture. It is one of the fields from which separation of the organic solvent by the membrane-separation method etc. also attracts attention, and inquires by the conventionally easy approach as an approach of separating or condensing the mixture (for example, mixture with which the boiling point is close with mixture etc. and separation by distillation contains the weak matter in difficult mixture, azeotropic mixture, and heat) which was not able to be separated.

[0003] By the way, misgiving that some of organic halogenated compounds of the number of low carbon are toxic to the body has comparatively the organic substance which is dissolving underwater, for example, trihalomethane etc., and there are some carcinogenic is indicated to be. There is indication that such an organic halogenated compound is contained in tap water in recent years in many cases, and establishment of an approach which removes this completely is desired.

[0004] Although the pervaporation method attracts attention recently as an approach of separating organic mixture As a demarcation membrane which the pervaporation method which used the demarcation membrane also for removal of the organic substance which dissolves underwater is tried, and can be used for this approach The acrylic ester-acrylic-acid copolymer film (**** et al., the 12th annual convention of the Membrane Society of Japan, 1990), a denaturation silicone compound hollow fiber (the Ito chapters, the 22nd time autumn convention of the Society of Chemical Engineers, Japan, 1989), etc. are proposed. However, by these film, discontinuous-selection nature cannot separate organic compounds, such as ***** rare ** trihalomethane, underwater certainly rather than can be enough.

[0005] Moreover, JP,3-98632,A carries out the graft polymerization of the acrylic monomer to the polyethylene fine porosity film, and is indicating the demarcation membrane which comes to be filled with the pore of the fine porosity film with an acrylic graft polymer substantially. Although this demarcation membrane can separate a specific component from the mixture (for example, benzene, a cyclohexane, chloroform and n-hexane, methyl acetate and a cyclohexane, an acetone, a carbon tetrachloride, etc.) of the organic substance good Even if it uses the demarcation membrane which carried out the graft polymerization of the acrylic monomer to the polyethylene fine porosity film at

random, and was substantially filled with the pore with the acrylic graft polymer according to this invention person's etc. research It turned out that separation removal of the organic halogenated compounds including trihalomethane, such as an organic compound contained underwater, especially chloroform, cannot be carried out certainly.

[0006] The graft polymer which is full of it in the pore of the fine porosity film when using underwater the so-called filling polymerization film make the pore of the fine porosity film which consists of polyethylene etc. by plasma graft polymerization etc. come to be [film] full of a graft polymer for separation removal of organic compounds, such as a ***** rare ***** halogenated compound, needs to have good compatibility to the organic compound for separation while being nonaqueous solubility. That is, the monomer which carries out graft polymerization turns into a nonaqueous solubility monomer fundamentally.

[0007] By the way, although it is necessary to form an almost uniform graft polymer in the fine porosity film (pore section) in order to manufacture the demarcation membrane excellent in separability ability etc. by plasma graft polymerization, it is desirable to contact the fine porosity film which made this solution generate a radical using the solution which dissolved the monomer which carries out graft polymerization in homogeneity for that purpose. According to this invention person's etc. research, it is desirable to use the water solution of the monomer which carries out especially graft polymerization. However, since the monomer which carries out graft polymerization was a nonaqueous solubility monomer as mentioned above, good graft polymerization was not able to be performed by the old approach.

[0008] Therefore, the purpose of this invention is offering the demarcation membrane which can remove alternatively the organic compound which is dissolving underwater.

[0009] Moreover, another purpose of this invention is offering the approach such a demarcation membrane's being manufactured.

[0010] Furthermore, another purpose of this invention is offering the approach of removing alternatively the organic compound which is dissolving underwater, using the above-mentioned demarcation membrane.

[0011]

[Means for Solving the Problem] In view of the above-mentioned purpose, using the polyethylene fine porosity film as a base material, wholeheartedly, by carrying out the plasma graft polymerization of the nonaqueous solubility monomer to this film, this invention person discovered that the demarcation membrane substantially filled with pore with the graft polymer of a nonaqueous solubility monomer, then the organic compound which exists underwater could be penetrated alternatively, and it could dissociate with water, and completed this invention as a result of research.

[0012] That is, the demarcation membrane of this invention is characterized by having carried out the plasma graft polymerization of the nonaqueous solubility monomer to the polyethylene fine porosity film, having had it in it, and being substantially filled with the pore of said fine porosity film with the graft polymer of said nonaqueous solubility monomer.

[0013] Moreover, the approach of this invention that the above-mentioned demarcation membrane can be manufactured (a) Add a nonaqueous solubility monomer and a surface active agent to water, and the emulsion liquid of a uniform nonaqueous solubility monomer is prepared. (b) It is characterized by contacting the polyethylene fine porosity film which the plasma was irradiated [film] and made the radical generate in said emulsion liquid, having it, and being substantially filled with the pore of said polyethylene fine porosity film with the graft polymer of said nonaqueous solubility monomer.

[0014] Furthermore, the approach of this invention of separating alternatively the organic compound contained underwater is characterized by separating alternatively the organic compound which has compatibility in the graft polymer of said nonaqueous solubility monomer by the pervaporation method, the steamy transmission method, or reverse osmosis using the demarcation membrane which performs the plasma graft polymerization which used the nonaqueous solubility monomer on the polyethylene fine porosity film, and comes to be filled with the pore of said fine porosity film with the graft polymer of said nonaqueous solubility monomer on it substantially.

[0015] This invention is explained to a detail below. The demarcation membrane of this invention is explained first.

[0016] The demarcation membrane of this invention uses the polyethylene fine porosity film as a base material. Although what consists of ultra high molecular weight polyethylene and high density polyethylene can be used as polyethylene fine porosity film, it is good to use what consists of ultra high molecular weight polyethylene from a strong viewpoint.

[0017] The void content of the polyethylene fine porosity film is 35 - 90% of range more preferably 30 to 95%. When a void content comes for the permeability of the separation specified substance to be inadequate at less than 30% and exceeds 95% on the other hand, a membranous mechanical strength becomes small and is inferior to practicality.

[0018] Moreover, an average aperture is good to be within the limits of 0.005-1 micrometer. If the permeability of the specified substance of separation becomes that an average aperture is less than 0.005 micrometers inadequate and an average aperture exceeds 1 micrometer, separability ability will fall.

[0019] Furthermore, breaking strength 200kg/cm² It is good to consider as the above. Breaking strength 200kg/cm² The deformation resistance over the swelling at the time of a separation object dissolving in the graft polymer formed in the pore of the polyethylene fine porosity film becomes enough [considering as the above].

[0020] in addition, the thickness of the polyethylene fine porosity film -- desirable -- 0.1-50 micrometers -- more -- desirable -- It is 0.2-25 micrometers. Thickness It is difficult for a membranous mechanical strength to be small and to present practical use in less than 0.1 micrometers. On the other hand, when exceeding 50 micrometers, it is too thick, and penetrable ability is reduced and it is not desirable.

[0021] the crystalline line which ultra high molecular weight polyethylene becomes from the homopolymer of ethylene, or the copolymer of ethylene and the alpha olefin not more than 10 mol % -- ultra high molecular weight polyethylene -- it is -- the molecular weight -- weight average molecular weight -- 5x10⁵ or more -- desirable -- 1x10⁶ to 1x10⁷ it is . The weight average molecular weight of ultra high molecular weight polyethylene influences the mechanical strength of the demarcation membrane obtained. Weight average molecular weight is 5x10⁵. In the following, it is ultra-thin and the demarcation membrane of high intensity is not obtained. On the other hand, especially for the upper limit of weight average molecular weight, although not limited, weight average molecular weight is 1x10⁷. Since thin-film-izing by extension processing is difficult when it exceeds, it is not desirable.

[0022] In the case of the ultra-high-molecular-weight-polyethylene fine porosity film, other things which blended the polyethylene of low molecular weight comparatively can be used for ultra high molecular weight polyethylene. In this case, weight average molecular weight is 7x10⁵. The above ultra high molecular weight polyethylene is contained 1% of the weight or more, and weight average molecular weight/number average molecular weight is 10-300. What consists of a polyethylene constituent is desirable.

[0023] the weight average molecular weight/number average molecular weight of the above-mentioned polyethylene constituent -- 10-300 -- it is 12-250 preferably. Since average chain length has large weight average molecular weight/number average molecular weight and the tangle consistency of the chains at the time of the dissolution becomes high less than by ten, preparation of a high concentration solution is difficult. Moreover, 300 If it exceeds, at the time of extension, fracture of a low molecular weight constituent will take place, and the reinforcement of the whole film will fall.

[0024] In addition, weight average molecular weight/number average molecular weight is used as a scale of molecular weight distribution, and the width of face of molecular weight distribution is expanded, so that the ratio of this molecular weight becomes large. That is, in the constituent which consists of polyethylene with which weight average molecular weight differs, it is shown that the difference of weight average molecular weight is so small that the difference of the weight average molecular weight of the polyethylene blended, so that the ratio of the molecular weight of a constituent is large is small greatly.

[0025] The content in the polyethylene constituent of this ultra high molecular weight polyethylene is the whole polyethylene constituent 100 It considers as weight % and is 1 % of the weight or more. A

tangle of the chain of the ultra high molecular weight polyethylene which the content of ultra high molecular weight polyethylene contributes to ductile improvement at less than 1 % of the weight is hardly formed, and cannot obtain the fine porosity film of high intensity. On the other hand, although especially an upper limit is not restrictive, if it exceeds 90 % of the weight, achievement of high-concentration-izing of a polyethylene solution made into the purpose will become difficult.

[0026] Moreover, for polyethylene other than the ultra high molecular weight polyethylene in a polyethylene constituent, weight average molecular weight is 7×10^5 . Although it is the thing of the following, as a minimum of molecular weight, it is 1×10^4 . The above thing is desirable. Weight average molecular weight is 1×10^4 . If the polyethylene of the following is used, since fracture will tend to take place at the time of extension and the target fine porosity film will not be obtained, it is not desirable. Especially weight average molecular weight is 1×10^5 . It is 7×10^5 above. It is desirable to blend the polyethylene of the following with ultra high molecular weight polyethylene.

[0027] Although the above-mentioned ultra high molecular weight polyethylene and a thing of the same kind are mentioned as such polyethylene, especially high density polyethylene is desirable.

[0028] In addition, on each above-mentioned polyethylene fine porosity film, various additives, such as an anti-oxidant, an ultraviolet ray absorbent, lubricant, an anti blocking agent, a pigment, a color, and an inorganic bulking agent, can be added also in any in the range which does not spoil the purpose of this invention if needed.

[0029] Here, the manufacture approach of the ultra-high-molecular-weight-polyethylene fine porosity film is explained. In the case of the fine porosity film which consists of an ultra-high-molecular-weight-polyethylene independent first, it can manufacture by the approach of a publication to JP,60-242035,A.

[0030] Next, in the case of the fine porosity film which consists of a polyethylene constituent which comes to blend the polyethylene of low molecular weight with ultra high molecular weight polyethylene comparatively, it can manufacture by the following approaches.

[0031] First, a high concentration solution is prepared by carrying out the heating dissolution of the above-mentioned polyethylene constituent at a solvent. As this solvent, especially if a polyethylene constituent can fully be dissolved, it will not be limited, but it is the same as the thing of a publication to above-mentioned JP,60-242035,A, and good for it. The heating dissolution is performed stirring at the temperature which a polyethylene constituent dissolves completely in a solvent. Although the temperature changes with the polymers and solvents to be used, the range of 140 - 250 °C is desirable. Moreover, the concentration of a polyethylene constituent solution is 10 - 40 % of the weight preferably ten to 50% of the weight.

[0032] Next, the heating solution of this polyethylene constituent is extruded and fabricated from a dice. a dice -- usually -- a rectangular mouthpiece -- although the sheet dice which carried out the configuration is used, a double cylinder-like hollow system dice, an inflation dice, etc. can be used. The dice gap at the time of using a sheet dice is usually 0.1-5mm, and is heated by 140 - 250 °C at the time of extrusion molding. Under the present circumstances, an extrusion rate is usually a part for part [for 20-30cm/, and 2-3m/.

[0033] Thus, the solution extruded from the dice is fabricated by the gel object by cooling. Below for setting temperature, cooling is 50degree-C/at least. It is desirable to carry out the rate more than a part.

[0034] Next, this gel moldings is extended. Extension heats a gel moldings and the combination of the usual tenter method, the rolling method, a tubular film process, the rolling-out methods, or these approaches performs it for a predetermined scale factor like the above. Biaxial extension is desirable, and although any of in-every-direction coincidence extension or serially extension are sufficient, especially coincidence biaxial extension is desirable.

[0035] Extension temperature is the range under of crystal distribution temperature to a crystalline melting point preferably the melting point of +10 degrees C or less of a polyethylene constituent. For example, 90-140 degrees C is the range of 100 - 130 °C more preferably.

[0036] In the demarcation membrane of this invention, the graft polymer of the polyethylene fine porosity film mentioned above which consists of a nonaqueous solubility monomer is formed in the pore internal surface at least, and it has the structure with which this graft polymer filled pore substantially.

The graft polymerization of a nonaqueous solubility monomer is performed by the plasma graft polymerization method so that it may mention later.

[0037] By this invention, since it is making into the key objective to obtain the demarcation membrane which separates alternatively the organic compound which exists underwater, as a monomer which carries out graft polymerization, what has good compatibility to a separation object is chosen and used by nonaqueous solubility (that is, it does not swell in water and does not let water pass). Of course, graft polymerization is possible for a monomer. When separation objects are the organic compound contained underwater, especially an organic halogenated compound (a carbon number is the organic halogenated compound of the two or less number of low carbon), what has compatibility in an organic halogenated compound as a nonaqueous solubility monomer which carries out graft polymerization is chosen. Specifically, the acrylic monomer of nonaqueous solubility, an methacrylic system monomer, a styrene system monomer, etc. can be used as a nonaqueous solubility monomer. It is desirable to use the acrylic monomer of nonaqueous solubility especially.

[0038] As an acrylic monomer of nonaqueous solubility, ethyl methacrylate, methacrylic-acid butyl, 2-ethylhexyl methacrylate, etc. are mentioned as an ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, acrylic-acid benzyl, and an methacrylic system monomer. Moreover, styrene, alpha methyl styrene, etc. can be used as a styrene system monomer.

[0039] In this invention, although a graft polymer is made to form in the pore internal surface of the fine porosity film as above-mentioned, a plasma graft polymerization method is used for this. By the plasma graft polymerization method, after irradiating the plasma at the fine porosity film made from ultra high molecular weight polyethylene and making a radical generate, it is made to contact by the approach of mentioning the above-mentioned nonaqueous solubility monomer later on the fine porosity film, and the graft polymerization of the nonaqueous solubility monomer is carried out.

[0040] As plasma graft polymerization, although there are a vapor-phase-polymerization method and a liquid phase polymerization method, a liquid phase polymerization method is desirable for carrying out the graft polymerization of the monomer.

[0041] The graft polymerization of the nonaqueous solubility monomer can be carried out even to a pore internal surface by generating and carrying out the graft polymerization of the radical to the way of the fine porosity film used as a base material instead of the nonaqueous solubility monomer by which graft polymerization is carried out. In addition, although a graft polymer is generated by front faces other than the pore internal surface of the ultra-high-molecular-weight-polyethylene fine porosity film, lessening as much as possible is desirable.

[0042] Drawing 1 is the partial cross-section perspective view showing notionally the process which carries out the plasma graft polymerization of the monomer to the polyethylene fine porosity film 2, and is used as the demarcation membrane of this invention. (a) it is alike, and the polyethylene fine porosity film 2 has much pores 3 which penetrate the film so that it may be shown. Plasma graft polymerization is performed on this fine porosity film, and that front face is made to carry out the graft polymerization of two or more monomers. (b) of drawing 1 By the demarcation membrane 1, the polymer 4 which carried out graft polymerization is formed not only in the film surface section of the fine porosity film but in the internal surface of pore 3, and one mode of the film with which pore 3 was substantially filled up with the graft polymer 4 is shown so that it may be shown. In addition, although the graft polymer 4 is formed in both sides of the fine porosity film 2 in this drawing, as for this invention, the graft polymer 4 may be formed even in one side of not only this but the polyethylene fine porosity film 2, and the part in pore.

[0043] In addition, the homopolymer by which the byproduction was carried out in process of plasma graft polymerization is completely flushed using solvents, such as toluene, and leaves only a graft polymer on the front face of the polyethylene fine porosity film (a pore internal surface and film front face).

[0044] Plasma graft polymerization specifically consists of the following processes.

[0045] (a) Make inorganic or an organic solvent dissolve or suspend the nonaqueous solubility monomer which carries out graft polymerization, and prepare the homogeneity solution of a nonaqueous solubility

monomer. Although it is desirable to use the water solution of the monomer which carries out a polymerization in plasma graft polymerization generally, since the monomer used by this invention is the thing of nonaqueous solubility, by the approach of this invention, first, it adds a nonaqueous solubility monomer in water, and prepares the emulsion liquid of a nonaqueous solubility monomer. At this time, a surface active agent is added further and the uniform emulsion liquid of a nonaqueous solubility monomer is prepared. That of 0.1 - 100 weight ***** is good for the water 100 weight section which contains a surfactant 0.1 to 50% of the weight in preparation of this emulsion liquid in a nonaqueous solubility monomer. And it is good to consider as the emulsion liquid which stirs the liquid considered as the above-mentioned combination by supersonic vibration, and a nonaqueous solubility monomer comes to distribute to homogeneity. Emulsion liquid with the amount of a surface active agent good at less than 0.1 % of the weight is not obtained, and a uniform graft polymer cannot be formed in a fine porosity film front face. On the other hand, if 50 % of the weight is exceeded, a possibility of checking graft polymerization nature will arise. Moreover, the amount of a nonaqueous solubility monomer cannot form the graft polymer of sufficient amount for the pore of the fine porosity film under in the 0.1 weight sections to the water 100 weight section containing a surfactant. On the other hand, if the amount of a nonaqueous solubility monomer exceeds the 100 weight sections, control of a lap becomes difficult, a polymer is formed also in film front faces other than a pore internal surface, and it is not desirable.

[0046] (b) the emulsion liquid which performed plasma treatment for 1 - 1000 seconds to the fine porosity film, and the front face (a pore internal surface is included) of the polyethylene fine porosity film was made to generate a radical, and usually described above this polyethylene fine porosity film with the frequency of 10-30MHz, and outputs 1-1000W under existence of gas, such as an argon with which a pressure serves as 10⁻² - 10mbar, helium, nitrogen, and air, -- ** -- make it contact It is good to specifically immerse the polyethylene fine porosity film which made the above-mentioned emulsion liquid generate a radical. In addition, carrying out bubbling of nitrogen gas, the argon gas, etc., this actuation is 20-100 **, and is good to carry out for 1 minute - several days.

[0047] (c) Next, by toluene, a xylene, etc., wash the obtained fine porosity film for about 1 hour, and dry it.

[0048] By the plasma graft polymerization method shown above, the demarcation membrane of the purpose which blockaded the pore of the fine porosity film substantially with the graft polymer can be obtained. Since plasma graft polymerization happens only in the surface section of the polyethylene fine porosity film, a film base material is not degraded. Moreover, since it has combined with the film base material chemically, a graft polymer does not start aging.

[0049] In the demarcation membrane of this invention, it is required to fill the graft polymer with the pore of the polyethylene fine porosity film which is a film base material substantially. The graft polymer filled with pore incorporates the specific component of liquid mixture alternatively, and makes it penetrate to the membranous opposite side. If the void content of the polyethylene fine porosity film is made high, the amount of the matter (it dissociates) which penetrates the graft polymer in pore also increases, and efficient separation can be carried out. Moreover, since the swelling of a graft polymer is stopped with the polyethylene fine porosity film, the reinforcement as the whole film does not fall.

[0050] Next, the separation approach using the demarcation membrane of this invention mentioned above is explained.

[0051] By the approach of this invention, the organic compound underwater contained by the pervaporation method, a steamy transmission method, or reverse osmosis is separated using the demarcation membrane of this invention explained in full detail until now. The pervaporation method in an approach, the steamy transmission method, or the reverse osmosis of this invention is the same as that of the well-known pervaporation method, a steamy transmission method, or reverse osmosis fundamentally, supplies the mixed-liquor object or the steam (the water or the steam containing an organic compound) which separates the demarcation membrane of this invention and serves as a candidate for separation at a primary side, makes a secondary the low-tension side, and takes it out to a secondary by using one component (organic compound) of a mixed-liquor object as a gas or a liquid

except using the demarcation membrane of this invention.

[0052] although the application temperature requirement in the separation approach of this invention changes somewhat with separation objects -- usually -- 0-120 °C -- it considers as 10-100 °C preferably. Although the thermal resistance of the polyethylene fine porosity film becomes inadequate at the temperature exceeding 120 °C, and a problem arises in maintenance of a film configuration and it is based also on a separation object at less than 0 degree C, generally unit membrane area, thickness, and the amount of transparency per time amount decrease and are not desirable.

[0053] Moreover, a pressure range applicable to the separation approach of this invention is 200 kg/cm². It is 100 kg/cm² preferably hereafter. It is the following. 200 kg/cm² By the pressure which exceeds, configuration maintenance of the polyethylene fine porosity film becomes difficult.

[0054] When ethyl acrylate or butyl acrylate is used as a nonaqueous solubility monomer which carries out graft polymerization to the polyethylene fine porosity film, according to the approach of this invention, organic halogenated compounds, such as the chloroform which dissolved in water, a carbon tetrachloride, a trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, and a methylene chloride, can be separated good. In addition, organic compounds, such as dimethylformamide, dimethyl sulfoxide, an acetone, and a tetrahydrofuran, are also separable.

[0055]

[Example] The following concrete examples explain this invention to a detail further.

[0056] Examples 1 and 2 and example of reference 1 weight average molecular weight 2x10⁶, 6 micrometers of thickness, 46% of void contents, the average aperture of 0.02 micrometers, and breaking strength of 1300kg/cm² The plasma generator (product made from SAMUKO) was used for the ultra-high-molecular-weight-polyethylene fine porosity film (Tonen Chemical make: cut off molecular weight 200,000), and the plasma was irradiated. The conditions of the plasma treatment at this time are shown in Table 1.

[0057]

表 1

高周波出力	:	1 0 W
プラズマ照射時間	:	6 0 秒
雰囲気	:	アルゴンガス
雰囲気圧	:	0. 1 mbar

[0058] As shown in Table 2, in addition to water for sodium dodecylbenzenesulfonate (it omits Following SDS), and ethyl acrylate (it omits an example 1 and Following EA) or butyl acrylate (it omits an example 2 and Following BA), supersonic vibration was given and emulsion liquid was prepared. Moreover, emulsion liquid using methyl acrylate (it omits Following MA) comparatively easily dissolvable in water as an example 1 of reference was also prepared.

[0059] The ultra-high-molecular-weight-polyethylene fine porosity film which performed plasma treatment was immersed in the emulsion liquid (example 1) of EA, and the emulsion liquid (example 2) of BA, respectively, and graft polymerization was performed. Graft polymerization conditions (temperature, time amount) are shown in Table 2. Similarly the ultra-high-molecular-weight-polyethylene fine porosity film which performed plasma treatment was immersed in the emulsion liquid (example 1 of reference) of MA, and the graft polymerization of MA was performed.

[0060]

table 2 Example 1 Example 2 Example 1 of reference Monomer EA BA MA Monomer concentration (1) 5.0 10.0 3.0 SDS concentration (2) 30 100 - Temperature (degree C) 30 30 30 Time amount (minute) 30-90 30-180 The 10 - 30 table 2 notes (1) : A unit is water which is weight % and contains SDS 100 The amount (% of the weight) of the monomer added when considering as weight % is shown. (2) : units are g/liter and show the amount of SDS per 1l. of water.

[0061] The ultra-high-molecular-weight-polyethylene fine porosity film was washed in toluene after immersion one whole day and night, and it dried at the room temperature. Membranous weight was

measured after desiccation and the amount of graft polymerization was measured by change from early film weight. A result is shown in drawing 2.

[0062] Although there are most cases of MA and then they serve as order of EA and BA, the amount of graft polymerization per unit time amount can carry out the graft polymerization of the graft polymer of amount sufficient also by the case of BA to use graft polymerization reaction time as about 2 hours, then a demarcation membrane to the fine porosity film, so that drawing 2 may show.

[0063] Each obtained film became transparent after the reaction, and it checked that the hole in a base material was buried with the graft polymer. Moreover, the obtained polymerization film was analyzed by the Fourier transform mold IR method of a transparency mold and a total reflection mold, and it checked that EA, BA, or MA was carrying out graft polymerization within a pit as a result of the comparison with the presentation of the whole film, and a surface presentation.

[0064] Using this demarcation membrane, 0.1 - 0.3% of the weight of the chloroform water solution was used as supply liquid, and the separation trial of chloroform was performed by the pervaporation method. It is the following, and the amount (concentration) of the chloroform in the liquid (it is hereafter called permeate liquid) which penetrated supply liquid and a demarcation membrane was made and measured. First, the hexane extracted the chloroform in supply liquid and permeate liquid, this extract was applied to the gas chromatograph (FDI detector), and the quantum of the chloroform in each liquid was carried out. A result (relation between the chloroform concentration of supply liquid and the chloroform concentration of permeate liquid) is shown in drawing 3.

[0065] The graft polymerization film of MA condensed 0.12% of the weight of the chloroform water solution to 9.86 % of the weight by the graft polymerization film (example 1) of EA to water permeability being shown so that drawing 3 might show. Moreover, by the graft polymerization film (example 2) of BA, 0.11% of the weight of the chloroform water solution was condensed to 33.1 % of the weight.

[0066] Moreover, transparency flux (Q) was evaluated as unit time amount and permeate liquid weight per unit membrane area (kg/m² and hr). The relation between the chloroform concentration of supply liquid and transparency flux is shown in drawing 4.

[0067] The way of the graft polymerization film (example 1) of EA and the graft polymerization film (example 2) of BA showed bigger transparency flux than the graft polymerization film (example 1 of reference) of MA so that drawing 4 might show.

[0068]

[Effect of the Invention] The polyethylene fine porosity film is used for the demarcation membrane of this invention as a base material, and it has good bloating tendency-proof to organic solvent ****. When high density polyethylene and ultra high molecular weight polyethylene are used especially as polyethylene, a demarcation membrane is excellent in a mechanical strength and endurance. Moreover, good separation of repeatability can be performed.

[0069] In the demarcation membrane of this invention, since the graft polymer which consists of a nonaqueous solubility monomer blockades the inside of the pore of the fine porosity film substantially, a polymer and an affinitive liquid are separable with high selectivity by using the pervaporation method, a steamy transmission method, or reverse osmosis. Therefore, if ethyl acrylate and butyl acrylate are used as a nonaqueous solubility monomer, low carbon organic halogenated compounds, such as chloroform, are separable with high selectivity.

[0070] By the manufacture approach of the demarcation membrane of this invention, uniform emulsion liquid is prepared from a nonaqueous solubility monomer, a surface active agent, and water, graft polymerization is performed to the polyethylene fine porosity film using this emulsion liquid, a graft polymer is formed in the front face of the polyethylene fine porosity film at homogeneity, and the good demarcation membrane of separability ability can be manufactured.

[Translation done.]